



UV-LED TiO₂ photocatalytic oxidation of acetone vapor: Effect of high frequency controlled periodic illumination

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ABSTRACT

We investigated the effect of controlled periodic illumination on quantum efficiency of acetone vapor photocatalytic oxidation. It was demonstrated that quantum efficiency increases with the increase of light pulses frequency and decrease of the duty cycle and at some point reaches its maximum value which is equal to the quantum efficiency obtained under the same average photon flux. Several kinetic models were applied to the experimental data. The general conclusion was made that there are only two kinetically distinguishable active species on TiO₂ surface with the lifetimes in 10⁻³–10¹ s range.

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1. Introduction

Heterogeneous photocatalytic oxidation of organic compounds on TiO₂ is considered as one of the most promising ways of air and water treatment [1]. The usage of UV light-sources for TiO₂ excitation is one of the main drawback which hinders the commercialization of photocatalytic technologies. Another problem is the low quantum efficiencies (QE) of the photocatalytic processes. One of the approaches to increase quantum efficiency is the usage of controlled periodic illumination (CPI). Main controllable parameters during CPI experiments are the CPI period (τ) which equals to the sum of illuminating and dark times of the one pulse of light and the duty cycle (γ) which equals to the ratio of illuminating time to the CPI period (Fig. 1).

In the early work of Sczechowski et al. authors investigated the influence of duty cycle on the quantum efficiency of formate ions photocatalytic oxidation (PCO) in the TiO₂ water suspension [2]. Authors used specially designed channel photoreactor with laminar flow of TiO₂ water suspension. Duty cycle value was regulated by alumina foil which covered certain sections of channel photoreactor. It was demonstrated that decrease of duty cycle value from 1 (continuous illumination) to 0.05 resulted in the

increase of quantum efficiency from 4% to 20% although total PCO rate decreased by 5 times. Authors suggested that photoefficiency increases with CPI decrease due to lower intermediates concentration in the water suspension thus resulting in higher efficiency for the conversion of electron–hole pairs in the PCO process other than recombination or other redox processes that do not oxidize the organic. Later work of the same authors with a Taylor vortex photoreactor demonstrated the coinciding results [3].

The same reaction of HCOO[–] PCO in a rotating disk reactor under CPI conditions was investigated by Buechler et al. [4]. Illumination and dark times were controlled by mechanical shutter which could provide times as short as 0.1 s. It was demonstrated that at a light time of 0.6 s and a dark time of 2.0 s ($\gamma=0.23$) and a light intensity of 5.5 mW/cm² the photoefficiency increased from 5% during the continuous illumination experiments to 20% with CPI. However, at low light intensities ($I<0.5$ mW/cm²) CPI did not affect the photoefficiency. Authors supposed that dark time in CPI is allowing time for oxygen to diffuse to the surface in their reactor system. In the later work of the same authors [5] the photocatalytic oxidation of formate ion under CPI and continuous illumination of TiO₂ particles was compared in an annular slurry reactor and in a rotating disk reactor. The extended conclusion was made that either intraparticle diffusion in flocculated particles or mass transport of oxygen to the catalyst surface or combination of these processes responsible for QE increase under CPI conditions.

In the most recent study of CPI influence on the QE of the photocatalytic degradation of methyl orange, Tokode et al. used UV

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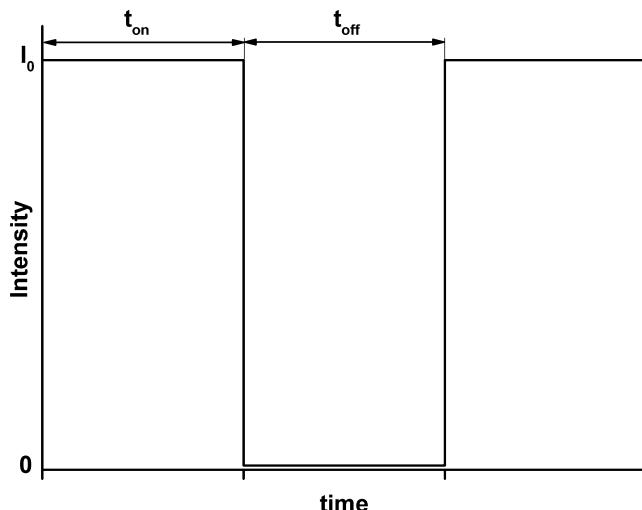


Fig. 1. Time profile of CPI pulses. Duty cycle, $\gamma = t_{\text{on}}/(t_{\text{on}} + t_{\text{off}})$; CPI period, $\tau = t_{\text{on}} + t_{\text{off}}$.

LED which provided rectangular impulses in the millisecond time regime [6]. It was demonstrated in the work that at the constant CPI period the quantum efficiency increases up to 3.5 times when duty cycle is equal to 0.08 if compared with continuous illumination and does not depend on the CPI frequency in the range of 0.1–10 Hz. The absence of frequency dependence could be explained by the fact, that CPI frequencies used in those experiments were too low and its possible influence could be hardly observed in this frequency range.

All the studies mentioned above explained increase in QE by diffusion and/or adsorption of reagents during the dark period. However those authors did not take into account that variation of duty cycle means variation in photon flux, which has a strong effect on the QE [7]. Therefore the effect of CPI on photocatalytic process cannot be investigated just in terms of duty cycle influence and investigation of frequency influence is also necessary.

Working with fixed duty cycle, Cornu et al. [8,9] investigated influence of t_{on} varying it in 0.0005–5 s range on methyl orange and formate photooxidation. Authors observed that QE changed stepwise at two different t_{on} values. Cornu associated these t_{on} values with the lifetimes of oxidizing and reducing intermediates since they strongly depended on pH of the reaction suspension. Those conclusions contradicted to the studies of Buechler and Szczekowski who explained increase in photoefficiency by mass transfer limitations.

The influence of CPI on the kinetics of gas-phase processes was not investigated as much. The only study for our knowledge was done by Buechler et al. [10]. Authors reported 1.8-fold increase in the apparent quantum yield ($t_{\text{on}} = 0.5$ s, $\gamma = 0.1$) in diffusional limited regime. As they increased flow rate, approaching kinetic limited regime, they observed no enhancement of quantum yield. In this way the conclusion was made that CPI effect can be explained by diffusional limitations in both gas and water purification.

From the above papers only Tokode with co-authors [6] used UV LED as CPI light source but with low frequency. Other researchers used mechanical shutter or specially designed reactors for periodic illumination. On the other hand modern UV LEDs are very powerful narrow-band devices with short relaxation times. So it is possible to obtain very stable high-frequency powerful rectangular light pulses for photocatalyst illumination.

In this paper we present the results of our investigation of the gas-phase acetone vapor photocatalytic oxidation under CPI. Equipment used in our experiment, such as 10 W UV LED (NICHIA,

$\lambda = 367$ nm) and self-made pulse generator, allowed us to obtain rectangular light pulses as short as 500 μ s. Dependence of QE on CPI period and duty cycle was approximated with several kinetic models and demonstrated a good fit to the experimental data. Its analysis suggests that there are two kinetically distinguishable active species on TiO_2 surface through which photooxidation proceeds.

2. Experimental

An experimental setup was designed to investigate the influence of the acetone vapor photocatalytic oxidation rate on the CPI parameters. The setup could be divided into two units: (1) UV LED control unit and (2) photocatalytic reactor and kinetic measurement control unit (Fig. 2).

2.1. UV LED control unit

The rectangular signal from pulse generator (1) was forwarded to the amplifier (2) powered by stabilized power supply unit (3). Thus formed rectangular pulses of current were used for the UV LED (4) power supply. To make sure that the UV LED's light pulses were of squared shape with the same maximum light intensity (I_0) we controlled the incident light by pulse photodiode (6) which was loaded on the resistor (7). Its resistance value was adjusted to $RL = 1.5\text{ k}\Omega$ in order to achieve the photodiode relaxation time (τ_{RC}) less than 150 ns because $\tau_{\text{RC}} = RL \cdot C_{\text{eff}} = 1500\text{ }\Omega \cdot 100\text{ pF} = 150\text{ ns}$, where C_{eff} is the effective capacity of the photodiode and connecting wires. Form of the initial current and incident light were monitored via oscilloscope (5) connected to the pulse generator (1) and resistor (7) respectively. In this way at any time we controlled the shapes of UV LED current and photodiode signal. The photodiode signal was the most informative CPI characteristic because its maximum value was proportional to the maximum light intensity (I_0) and its squared shape was used for the calculation of the duty cycle value. UV LED used in our experiments had a narrow wavelength peak at 366 nm (see supplementary data, Fig. SD1). It was verified that its spectrum is independent on the current and CPI frequency. The maximum frequency which provided almost rectangular pulses was $\sim 10\text{ kHz}$ (see supplementary data, Fig. SD2). Further increase of the frequency resulted in the distortion of light pulses due to dynamical characteristics of the UV LED and frequency characteristics of the amplifier (2).

Quartz condenser (9) formed parallel light beam. Passing through a quartz window (10) of the flow photocatalytic reactor (11) it provided the illumination of the TiO_2 powder which was deposited onto the glass support (12). Inlet air stream of the reactor was prepared in order to be able to adjust its volumetric flow rate, humidity and concentration of organic substrate.

2.2. Photocatalytic reactor and kinetic measurement control unit

Reaction mixture preparation module consists of air purifier (14) which removes CO_2 , water and mechanical particles from pressurized air. Purified air then was divided into three streams. Water saturated air (15) along with the dry one (16) proceeded to mixing chamber (20) through mass-flow controllers. The third stream on the way to the mixing chamber passed through the pressure reducer (17), saturator with acetone (18) and mass-flow controller (21). Thus the initial reaction mixture with desirable water and acetone vapor concentration was obtained and passed through the steel photocatalytic reactor (11) with circulation pump (13).

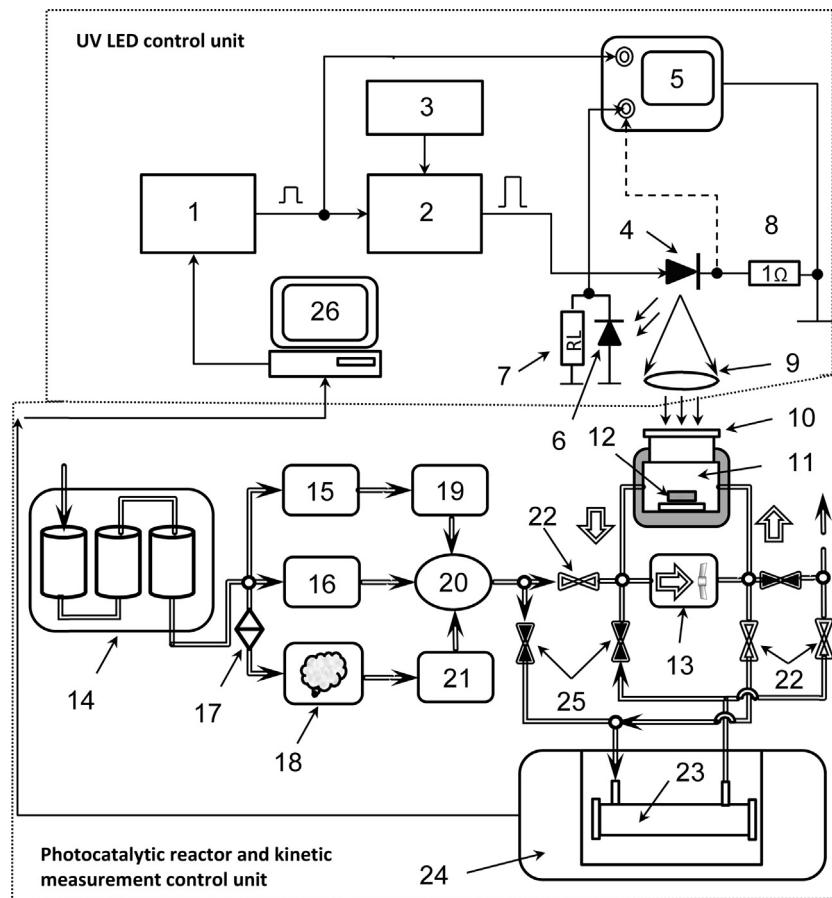


Fig. 2. Schematic diagram of the experimental set-up. *UV LED control unit*: (1) pulse generator (ATAKOM ANR-3122, Russia); (2) amplifier; (3) stabilized power supply unit (TES-88, Russia); (4) UV LED (Nichia NC4U133, Japan); (5) oscilloscope (Tektronix TDS 1012, USA); (6) pulse-photodiode (FD-256, Russia); (7) load resistor 1.5 kΩ; (8) UV LED current control resistor 1 Ω; (9) quartz condenser ($F=70$ mm). *Photocatalytic reactor and kinetic measurement control unit*: (1) photocatalytic flow-circulation reactor module; (10) quartz window; (11) steel thermostatic reactor; (12) photocatalyst sample; (13) circulation pump; (22 and 25) two-way valves; (23) IR long-path gas cell (IR Analysis, Inc., USA); (24) IR spectrometer FT-801 (Simex, Russia). (II) Reaction mixture preparation module; (14) air purifier; (15 and 18) saturators; (16, 19 and 21) mass-flow controllers; (17) pressure reducer.

Gas analysis was conducted with the long-path gas cell (23) installed in FTIR spectrometer (24). The rate of the reaction was calculated according to the formula:

$$W = \frac{\Delta C_{CO_2} \cdot U}{3}, \quad (1)$$

where ΔC_{CO_2} is the difference in CO_2 concentrations in the outlet and inlet of air streams of the reactor, and U is the volumetric flow rate ($L s^{-1}$). The QE was calculated according to the following formula:

$$\varphi_\gamma = \frac{W}{\gamma \cdot I_0}, \quad (2)$$

where I_0 is the incident photon flux corresponding to the maximum light intensity ($mol s^{-1}$) and γ is the duty cycle [11].

Special valve system with two operational modes was developed (Fig. 2). If white valves (22) are open and black valves (25) are closed then reaction mixture firstly passes the reactor and then comes into the long-path gas cell (23) for outlet air analysis. Switching of the all six valves results in that the inlet air stream is firstly comes into the FTIR spectrometer for analysis and then into the photocatalytic reactor. In this way the ΔCO_2 and the subsequent reaction rate (W) values were calculated.

Both control units were automated with LabView (National Instruments, USA) and operated via computer (26). Standard operational parameters were the following: acetone concentration – 600 ppm, temperature – 40 °C, relative humidity – 19 ± 2%,

volumetric flow rate (U) – 58 cm^3/min , maximum light intensity – 4.45 mW/cm^2 , TiO_2 (Degussa P25) deposited density – 1 mg/cm^2 , illuminated area – 9.1 cm^2 .

3. Results and discussion

3.1. Influence of CPI duty cycle on the kinetics of acetone vapor photooxidation

Firstly it was interesting to measure the dependence of PCO QE on the duty cycle value at the constant maximum light intensity I_0 . This dependence is presented in Fig. 3 (squares) for the relatively long CPI period $\tau = 120$ s. Bottom x-axis corresponds to the duty cycle value whereas upper x-axis corresponds to the average light intensity calculated as the product of $I_0 \cdot \gamma$. In the duty cycle range between 1 and 0.5 the quantum efficiency value estimated according to the formula (2) remains almost constant indicating that oxidation processes in the dark time of the period are negligible as compared to the PCO during the illumination period. At the same time the QE increases from 3% to 5.2% as the duty cycle value decreases from 0.5 to 0.05. It is indicating that the CO_2 quantity which is forming during the dark time of the period is comparable with that of forming during the illumination time. In other words some active species (AS) which were formed during illumination time and which are responsible for the acetone photomineralization to the CO_2 still work after the light was switched off and have

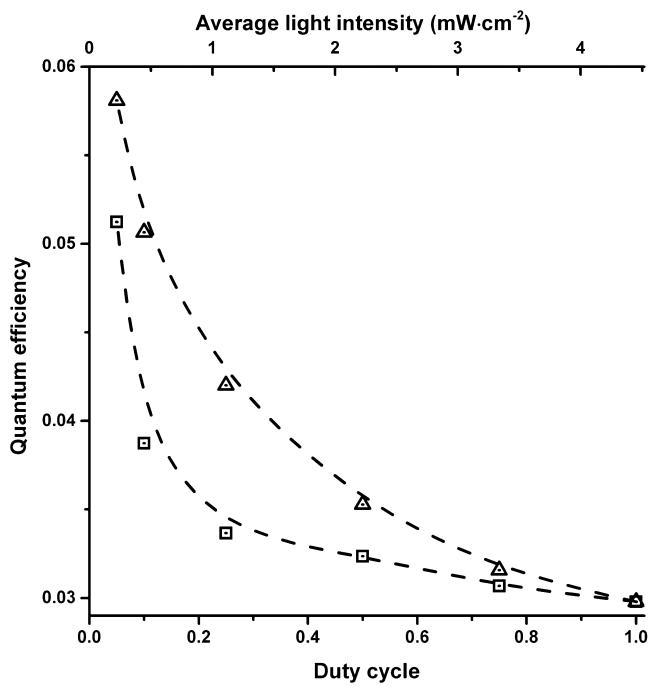


Fig. 3. The dependence of the QE of acetone vapor PCO: (□) on the duty cycle at the constant maximum light intensity $I_0 = 4.45 \text{ mW/cm}^2$ and $\tau = 120 \text{ s}$ or; (△) on the light intensity under continuous illumination. Upper scale equals to the bottom scale multiplied by the I_0 . Dashed lines correspond to the approximation results.

a lifetime as large as several seconds because the duty cycle effect becomes high at $\gamma = 0.1$ and $\tau = 120 \text{ s}$ ($t_{\text{on}} = 12 \text{ s}$ and $t_{\text{off}} = 108 \text{ s}$). Similar but less precise experiments were conducted by Sczechowski et al. in the early work [12] with the rotating disk photocatalytic reactor.

The dependence of the QE of acetone vapor PCO under the continuous illumination is also presented in Fig. 3 (up triangles). It could be seen from the figure that the QE under the same average light intensity in the continuous mode is always higher than in the CPI mode. In the work of Cornu et al. [8] the analogous result was demonstrated for formate PCO in the TiO_2 water suspension.

Taking into account the generally supposed mechanism of the photocatalytic oxidation process which includes the formation of photogenerated electron/hole pairs, their subsequent reaction with the adsorbed oxygen and water species, formation of highly reactive intermediates (active species or AS) and their interaction with the adsorbed substrate with the formation of reaction products, we examined the following differential equations system for the approximation of the experimental results:

$$\left\{ \begin{array}{l} \frac{dC}{dt} = \alpha \cdot I_0 - k_1 \cdot C - k_2 \cdot C^2 \\ W = \frac{d[\text{CO}_2]}{dt} = k_1 \cdot C \end{array} \right. , \quad (3)$$

with k_1 and k_2 the rate constants of the AS reaction in the rate determining and recombination reactions respectively. C is the AS concentration and αI_0 is the AS formation rate proportional to the maximum light intensity I_0 . In this model we implied that AS recombination rate is much higher than the PCO reaction rate ($k_1 C \ll k_2 C^2$), so under continuous illumination the steady-state AS concentration (C_{ss})

$$C_{\text{ss}} = \sqrt{\frac{\alpha \cdot I_0}{k_2}}, \quad (4)$$

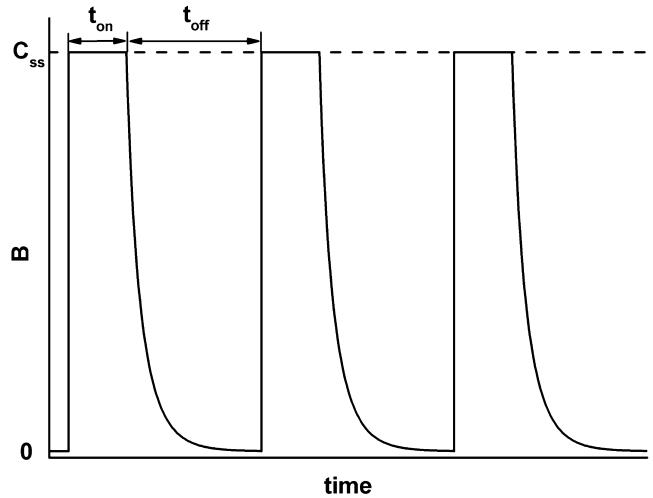


Fig. 4. Simulated profile of AS concentration on the photocatalyst surface as the function of the CPI parameters.

CO_2 formation rate W_0

$$W_0 = k_1 \cdot C_{\text{ss}}, \quad (5)$$

and the QE under continuous illumination $\varphi_0(I_0)$

$$\varphi_0(I_0) = \frac{W_0}{I_0} = k_1 \sqrt{\frac{\alpha}{k_2 \cdot I_0}}. \quad (6)$$

Here we used the simple second order kinetics of AS removal which gives that PCO rate is proportional to the light intensity in the power of 0.5, but according to the experimental results of Peral and Ollis the PCO rate is proportional to I_0^a , where $0.6 < a < 0.8$ [13]. In this way the QE is proportional to $I_0^{-0.5}$ according to Eq. (6) or to I_0^{a-1} according to the Peral and Ollis:

$$\varphi_{\text{PCO}} \sim I_0^{a-1} \quad (6')$$

In the case of CPI we supposed that AS concentration achieved steady-state value immediately after the beginning of illumination time (t_{on}) and then strongly but not in a moment decrease during dark time (t_{off}). It means that substrate oxidation by AS is continuing for some time during the dark period.

The average PCO rate under CPI (W_γ) could be estimated as the amount of evolved CO_2 divided by CPI period $\tau = t_{\text{on}} + t_{\text{off}}$:

$$W_\gamma = \frac{\Delta \text{CO}_{2,1} + \Delta \text{CO}_{2,2}}{\tau}, \quad (7)$$

where $\Delta \text{CO}_{2,1}$ and $\Delta \text{CO}_{2,2}$ are the amount of CO_2 evolved during t_{on} and t_{off} parts of CPI period. Assuming that the steady-state concentration (C_{ss}) is reached quickly we could estimate the $\Delta \text{CO}_{2,1}$ using Eq. (5) as

$$\Delta \text{CO}_{2,1} = W_0 \cdot t_{\text{on}}. \quad (8)$$

The $\Delta \text{CO}_{2,2}$ could be estimated as the time integral of Eq. (5):

$$\Delta \text{CO}_{2,2} = k_1 \int_0^{t_{\text{off}}} C \, dt. \quad (9)$$

The decrease of AS concentration during t_{off} part of the period is describing by second order kinetics of AS recombination with C_{ss} being an initial concentration (Fig. 4, interval t_{off}). Here we supposed that recombination rate is much higher than oxidation rate, so we neglected AS death via oxidation reaction:

$$\frac{1}{C} - \frac{1}{C_{\text{ss}}} = 2k_2 \cdot t. \quad (10)$$

Substituting Eq. (10) in Eq. (9) with subsequent integration gives the following expression:

$$\Delta CO_{2,2} = k_1 \int_0^{t_{\text{off}}} \frac{1}{(1/C_{\text{ss}}) + 2k_2 \cdot t} dt = \frac{k_1}{2k_2} \cdot \ln(1 + 2k_2 \cdot C_{\text{ss}} \cdot t_{\text{off}}), \quad (11)$$

Finally, using Eq. (4) for C_{ss} , Eq. (7) for W_y and Eq. (2) for QE the following expression for quantum efficiency under CPI could be obtained:

$$\varphi_y(I_0) = \varphi_0(I_0) + \frac{(k_1/2k_2) \cdot \ln \left[1 + 2\sqrt{\alpha \cdot k_2 \cdot I_0} \cdot (1 - \gamma)\tau \right]}{\gamma \cdot \tau \cdot I_0}. \quad (12)$$

Three conclusions could be made from Eq. (12):

- (1) QE under the CPI conditions $\varphi_y(I_0)$ is always higher than QE $\varphi_0(I_0)$ under the continuous illumination of the same maximum light intensity I_0 .
- (2) The lower is the duty cycle value γ the higher is QE $\varphi_y(I_0)$.
- (3) The lower is the CPI period τ the higher is QE $\varphi_y(I_0)$ value.

This statement implies that at very high CPI frequencies the AS concentration will approach to a certain steady-state value which will be the same as under the continuous illumination of γI_0 maximum light intensity. In other words the following statement is true:

$$\lim_{\tau \rightarrow 0} \varphi_y(I_0) = \varphi_0(\gamma \cdot I_0). \quad (13)$$

Eq. (12) for $\varphi_y(I_0)$ has a limiting value at $\tau \rightarrow 0$ but it is higher than $\varphi_0(\gamma I_0)$ by the factor of $\sqrt{\gamma}$ because we used relatively rough approximations when calculated $\varphi_y(I_0)$ QE. In particular, we assumed that steady-state concentration of AS was achieved immediately after the beginning of the illumination part of the period but in practice it takes a certain time. So at the very low τ values steady-state concentration of AS will not be achieved at all and the experimental QE value will be lower and will correspond to Eq. (13).

Dashed lines in Fig. 3 correspond to the approximation of experimental data points with Eq. (6') and Eq. (12) for continuous illumination and CPI respectively.

3.2. Influence of CPI period on the kinetics of acetone vapor photooxidation

Experiments of the previous section were based on changing duty cycle, i.e. varying average photon flux. It is well known and demonstrated in previously cited papers that QE depends on light intensity, so the fact that QE under CPI depends on duty cycle is not some extraordinary result. That is why CPI period experiments draw the most of our interest. By changing frequency of CPI at the fixed duty cycle we observe how photocatalytic system responds to the way we provide the same amount of energy. And in this case obtained dependencies are not disguised by the influence of illumination intensity on QE.

Results of CPI period experiment are presented in Fig. 6; duty cycle remained constant and equal to 0.5. Dashed lines mark QE under continuous illumination of the same maximum I_0 (lower horizontal line) and average γI_0 (upper horizontal line) light intensities. QE changes stepwise at two values of CPI period and reaches its maximum value equal to QE under the same average photon flux. Similar results were obtained by Cornu et al. for the formate and methyl orange oxidation [8,9]. It is obvious that presented results could not be described by simple kinetic model with one type of AS in the previous section (Eq. (3)), so we examined a new one.

Firstly we suggested that elementary kinetic scheme involving only reaction with the organic substrate and recombination. As a result differential equations corresponding to the kinetics of active

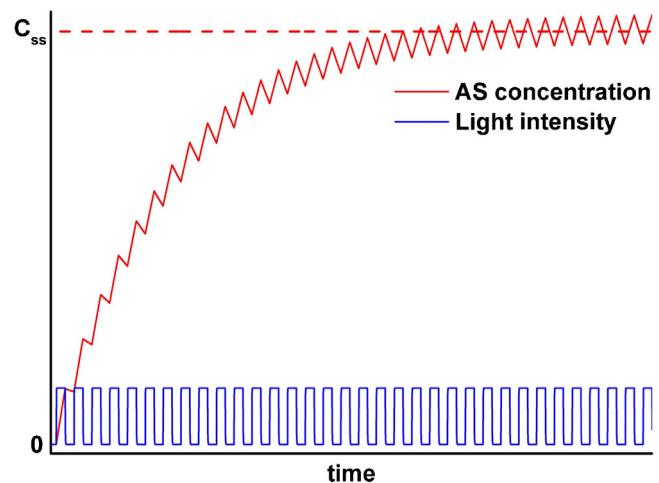


Fig. 5. Simulated AS concentration after switching-on intermittent illumination. Dashed line correspond to steady-state concentration under light intensity $I = 0.5I_0$.

species in the light (C_1) and dark (C_2) time became looking in the following way:

$$\begin{cases} \frac{dC_1}{dt} = \alpha \cdot I_0 - k_1 \cdot C - k_2 \cdot C^2, & t \in [0; \gamma \cdot \tau] \\ \frac{dC_2}{dt} = -k_1 \cdot C - k_2 \cdot C^2, & t \in [\gamma \cdot \tau; \tau] \end{cases}. \quad (14)$$

At the moment of turning on modulated illumination, concentration of AS begins to grow then fall and so on (Fig. 5). Finally system comes to pseudo steady state, i.e. rate of the PCO reaches its steady-state value, which we actually measure in the kinetic experiments. For this reason integrating equations (14) specific initial conditions should be taken into account:

$$C_1(0) = C_2(\tau); \quad C_1(\gamma \cdot \tau) = C_2(\gamma \cdot \tau). \quad (15)$$

According to the law of mass action instant rate of substrate oxidation is proportional to the AS concentration:

$$W = -\frac{dS}{dt} = k \cdot [C] \quad (16)$$

where S is the product concentration.

The total amount of oxidized substrate during one CPI period equals:

$$-\Delta S = k \cdot \int_0^{\tau} C dt = k \cdot \left[\int_0^{\gamma \cdot \tau} C_1 dt + \int_{\gamma \cdot \tau}^{\tau} C_2 dt \right] \quad (17)$$

The following equation gives the dependence of quantum efficiency under intermittent illumination on the CPI period and duty cycle:

$$\begin{aligned} \varphi(\tau, \gamma) &= \frac{\langle W \rangle}{\langle I \rangle} = -\frac{1}{\gamma \cdot I_0} \cdot \frac{\Delta S}{\Delta t} \\ &= \frac{1}{\gamma \cdot I_0} \cdot \frac{k_1 \cdot \left[\int_0^{\gamma \cdot \tau} C_1 dt + \int_{\gamma \cdot \tau}^{\tau} C_2 dt \right]}{\tau} \end{aligned} \quad (18)$$

Since analytical form for Eq. (18) is rather big it is listed in the supplementary data. Simulated dependence of the QE on CPI frequency is presented in Fig. 7. If to compare with experimental data presented in Fig. 6 it is clear that theoretical curve has one step whereas experimental dependence has two steps. This led us to consider kinetic scheme with two active species having different life times (see supplementary data). We followed procedure which was similar to the mentioned above, and its result with fitted parameters is presented in Fig. 6. Obtained values of constants were

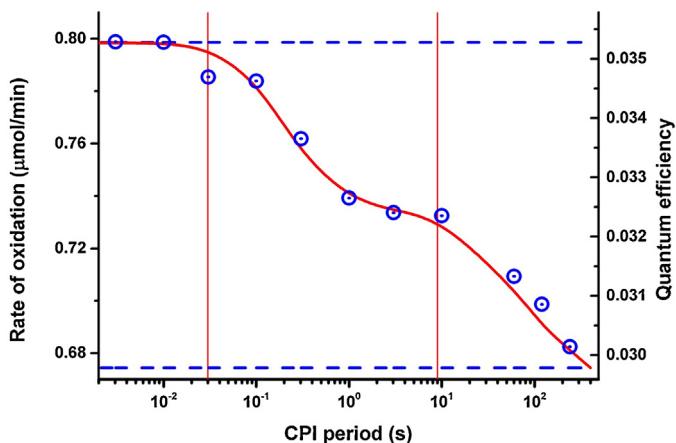


Fig. 6. Acetone vapor photocatalytic oxidation QE vs. CPI period at duty cycle 0.5. Circles – experiment; solid curve – model. Vertical lines mark calculated lifetimes of active species.

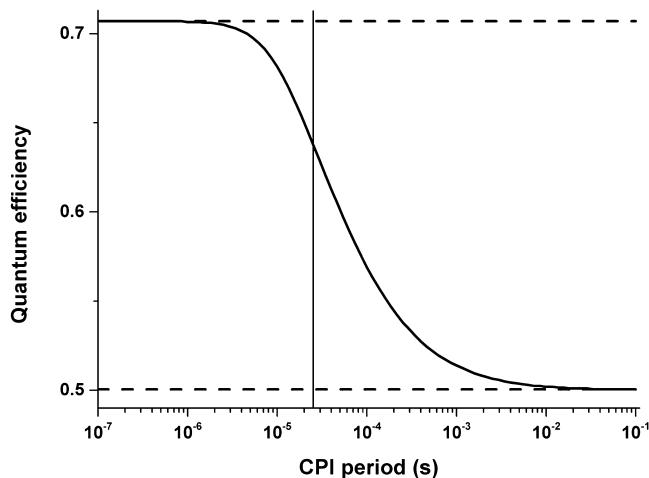


Fig. 7. Simulated dependence of the QE on the CPI period.

used to calculate the AS lifetimes (marked vertical lines) according to the following formula:

$$\tau_L = \frac{\int_0^\infty C(t) dt}{C_{ss}}, \quad (19)$$

where C_{ss} is the steady-state concentration of AS under constant illumination with light intensity equals I_0 .

With the values of fitted parameters we estimated AS lifetimes of 3×10^{-2} s and 9 s. These lifetimes could be associated with OH^\bullet and O_2^\bullet species respectively, since they are similar to ones obtained by independent methods. For example, Ishibashi et al. [14] investigated chemiluminescence response of TiO_2 film in air and found that there are two species with characteristic times 3 s and 50 s. Okuda et al. [15] identified them on similar timescale with the help of transient grating technique.

At the CPI period of 10 ms experimental as well as simulated QE values reach its maximum equal to constant value obtained under constant illumination of the same average light intensity $I_0/2$ (Fig. 6). This phenomenon was previously demonstrated by Cornu et al. [8] and is obvious from Eq. (13). We did not manage to prove Eq. (13) analytically because of large mathematics but our simulation demonstrates that decrease of CPI period results in the reduced amplitude with which AS concentration oscillate near its steady state value (see supplementary data, Fig. SD3). And at some point, when period is much shorter than AS lifetime, photocatalytic

system cannot recognize in which form we provide the same amount of light, in periodic or continuous mode. Thus our experiments along with the kinetic model demonstrate that QE of photocatalytic process under CPI cannot exceed QE under continuous illumination.

4. Conclusion

We investigated the effect of CPI on the acetone vapor photocatalytic oxidation with commercial Degussa P25 photocatalyst. Duty cycle experiments revealed that QE strongly increases as duty cycle approaches small values. Such behavior is observed even at as long CPI period as 120 s indicating that AS lifetime is up to several seconds. This is in a good agreement with the studies of photocatalytic oxidation of various organic substrates under CPI.

The dependence of QE on the CPI period has the same features as for the formate and methyl orange oxidation in aqueous suspension [1,2]. Namely:

- There are two prominent transitions.
- The maximum of quantum efficiency under CPI equals the value obtained under continuous illumination with the same average light intensity.

Model involving two types of AS was developed and provided a good fit for the experimental results. Furthermore using of initial conditions allowed us to demonstrate that QE under CPI cannot exceed QE under continuous illumination with the same average photon flux. Hence the only practical application of CPI to increase PCO efficiency is its implementation in rotating disk reactors [16] where we have constant light intensity and could change CPI period by changing the disk rotation velocity.

Active species with lifetimes of 3×10^{-2} s and 9 s could be associated with OH^\bullet and O_2^\bullet species respectively.

The conclusion could be made that CPI experiments are a powerful tool for direct evaluation of lifetimes of reactive intermediates on TiO_2 surface during the photocatalytic process. Further experiments should be aimed on the combination of pulse laser techniques with CPI measurements in order to observe active species with lifetimes in the wide range.

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Appendix A. Nomenclature

$t_{\text{on}}, t_{\text{off}}$	time of light and dark CPI period respectively
γ	duty cycle
τ	CPI period
α	light absorbance
C_{ss}	steady state concentration of AS
k_1	rate constant of oxidation reaction
k_2	rate constant of second order recombination
φ_γ	quantum efficiency under CPI
φ_0	quantum efficiency under constant illumination
C_1, C_2	concentration of AS in light and dark CPI period respectively
t_L	lifetime of AS

$\langle W \rangle$, $\langle I \rangle$ average values of reaction rate W and light intensity I during the whole CPI period

Appendix B. Supplementary data

Supplementary material related to this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.07.034>.

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